CAAP Annual Report

Date of Report: *Sept. 30th, 2018*

Contract Number: *DTPH56-16-H-CAAP03*

Prepared for: *U.S. DOT Pipeline and Hazardous Materials Safety Administration*

Project Title: Development of New Multifunctional Composite Coatings for Preventing and Mitigating Internal Pipeline Corrosion

Prepared by: *North Dakota State University*

Contact Information: *Mr. Xingyu Wang, PhD student, Email: xingyu.wang@ndsu.edu, Phone: 701-231-7204; Miss. Mingli Li, PhD student, Email: mingli.li@ndsu.edu, Phone: 701-231-7204; Matthew Pearson, M.S. student (former undergraduate research assistant), Email: matthew.pearson@ndsu.edu, Phone: 701-231-7204; Dr. Zhibin Lin, Email:zhibin.lin@ndsu.edu, Phone: 717-231-7204; Dr. Dante Battocchi, Email: Dante.Battocchi@ndsu.edu, Phone: 701-231-6219; Dr. Xiaoning Qi, Email: xiaoning.qi@ndsu.edu, Phone: 701-231-6464*

For quarterly period ending: *Sept. 30th, 2018*

Business and Activity Section

(a) Generated Commitments

No changes to the existing agreement

Purchase made for nano-materials over this reporting period

Four high school students in this summer were recruited in the research group

(b) Status Update of Past Quarter Activities

The research activities in the second annual report are summarized by characterizing the nano-modified coatings and assess their long-term performance, high school student outreach, and associated dissemination, as summarized below.

Summary of Tasks 4 and 5 in characterization of the new coating systems and long-term durability stress tests.

6.1.1 Background

The current research shows a higher improvement of adhesion, abrasion resistance, and tensile properties in the nanocomposites. Meanwhile, our study has also focused on the synergetic effect of nano-fillers on hydrophobicity, mechanical, and electrical properties of polymer coatings. In the meantime, the contact angle test was performed on the abraded coating surfaces, and significant increases were observed in the composite with nanoparticle reinforcement.

As mentioned in the last report, the pigment volume concentration should also be considered as a variable in the experimental study. The purpose of testing the bulk density of each nanofiller in the solvent is to calculate the filler volume concentration so we can understand the relation between volume and weight of nanoparticles in the solvent. Fourier Transform Infrared Spectrometer (FTIR) was utilized to investigate cured epoxy and nanofiller/epoxy composites to address the probable reaction of the polymer with and without nanofillers.

6.1.2 Objectives in the second annual report

A comparative study and detailed accelerated durability tests were conducted to evaluate the performance of the nanofiller and their long-term degradation mechanism. As a part of the project, the dissemination of the current research efforts and findings in the national and state conferences, and high school outreach programs.

6.2.1 Experimental design

The study includes the following tasks:

- The bulk density for each type of nanofiller was measured to calculate filler volume concentration in nanocomposites.
- Fourier Transform Infrared Spectrometer (FTIR) analysis was conducted to study the chemical reaction in a polymer with and without nanofillers.
- Nanofiller reinforced polymer
- Meanwhile, an experimental study has been performed to understand how contact surface modification leads to a dramatically increased water repellency of nanocomposites.

Moreover, several new experimental technologies were introduced in this study which includes Scanning electron microscopy (SEM), Atomic force microscopy (AFM), and Fourier Transform Infrared Spectrometer (FTIR) Measurements. Unless changes were specified in the following section, the sample preparation procedures and test methods from the previous study were continually used in this study.

6.2.2 Bulk density of nanofiller in an organic solvent

The bulk density for each type of nanofiller was measured by the following procedure: about 1g of filler was weighted and added into a 50 ml volumetric flask (Figure 1), then fill the about half of the flask with an organic solvent (for example xylene). After removing the air bubbles, fill the flask completely with the solvent. The weights of the empty flask, filler, and the total weight (flask, filler, and solvent) were measured by weight scale with an accuracy of 0.1 mg.

Figure 1 50ml measuring flask for the density test

(a) GSE specimens with varying filler concentrations

Figure 2 is presenting a coated sample with each mixture. Considering the wide range of concentration in tested samples, so two masterbatches were prepared. Corrosion barrier performance, abrasion resistance, contact angle, adhesion and dogbone tensile test were performed to characterize the prepared samples.

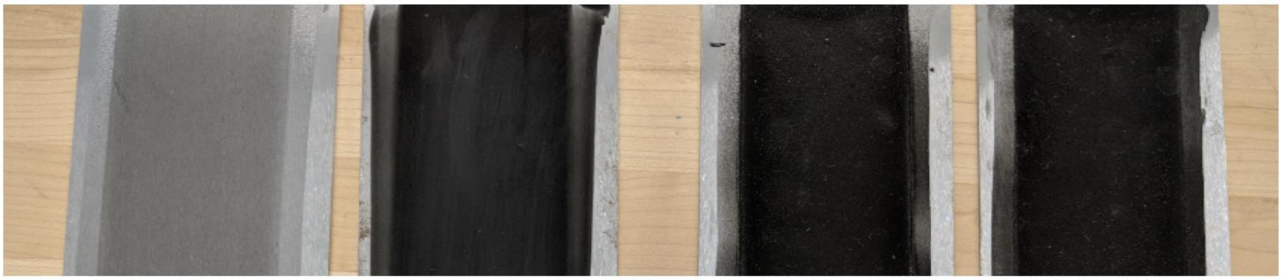

Figure 2 Samples

6.2.3 Salt Fog Corrosion Test

The influence of nanofillers on the corrosion behavior of exposed to salt fog was evaluated by ASTM B117 Salt Fog test. The ASTM B117, Salt Fog test, is an accelerated corrosion test which the samples are exposed to a corrosive environment in a fog chamber. The samples were maintained in a salt fog test environment during the test, and the salt solution should be a 5% NaCl solution with a PH ranged in 6.5 to 7.2. The temperature should be maintained at 35°C (95°F). EIS test was planned to be performed on each sample before the salt fog test, 24 hrs., 100 hrs., 200 hrs. and 500 hrs. after the test.

6.2.4 Fabrication of air sprayed specimens

The nanocomposite was selected to spray with high-volume low pressure (HVLP) spray gun, and the air sprayed samples were denoted as GSE1-50 (S). Adhesion, EIS, and contact angle tests were performed to characterize the sprayed samples.

6.2.5 Experimental technologies

Several experimental technologies were incorporated since the last annual report, which includes Scanning electron microscopy (SEM), Atomic force microscopy (AFM), and Fourier Transform Infrared Spectrometer (FTIR) Measurements.

6.3.1 Fourier Transform Infrared Spectrometer (FTIR) Measurements

FTIR analysis was conducted on all nanocomposites to understand the possible chemical reaction between polymer and nanofillers. The characteristic peaks (*Figure 3*) for all the samples are very similar which could be proof of that there is no chemical reaction between polymer and nanofillers.

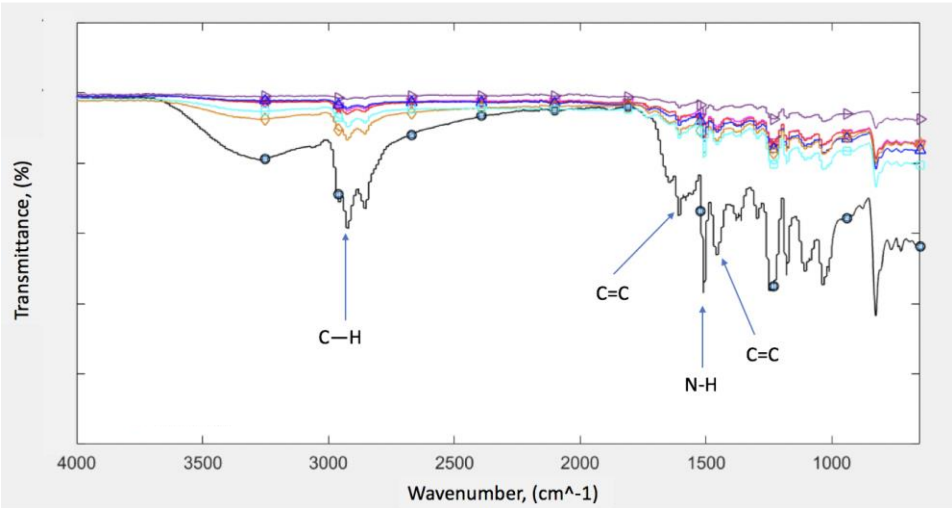

Figure 3 FTIR spectra for the samples

(a) Corrosion barrier performance: EIS

The corrosion barrier property is an important performance for evaluating the developed coatings. Potentiostatic EIS test has been used to measure the impedance of each sample group. The results of the EIS test for the samples were plotted in Figure 4. The result indicates that using selected nanoparticles can significantly reduce the corrosion rate of the polymer, and the improvement of the barrier performance is stronger than graphene nanoplatelets.

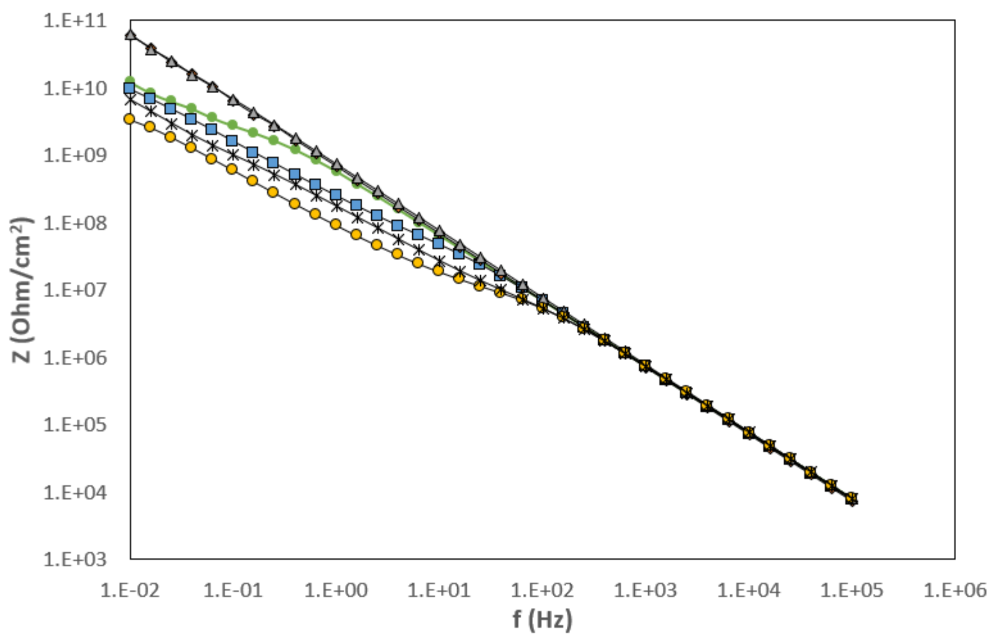

Figure 4 Impendence curve for the composites

(b) Dogbone tensile test

The tensile property of varied nanofiller reinforced coatings was determined by the dogbone tensile test, following ASTM D638. The nano-composites can be characterized by measuring maximum tensile stress, strain at failure, and Young's modulus in this test. The results indicate the selected nanoparticles have the highest reinforcement in the tensile strength, which could be contributed by the higher bonding strength to the subtract. Furthermore, a similar tendency was observed in Young's modulus curves.

(c) The adhesive bonding strength

The pull-off strength (adhesion) was measured by following ASTM D4541 to evaluate the tensile bond strength. Results show that there are high variances among different nanoparticles.

(d) Contact angle test

Figure 5 is shown an example of water contact test for a sample, which the contact angle was decreased to 16 degrees. This result indicates that there is no improvement of the hydrophobicity of the surface.

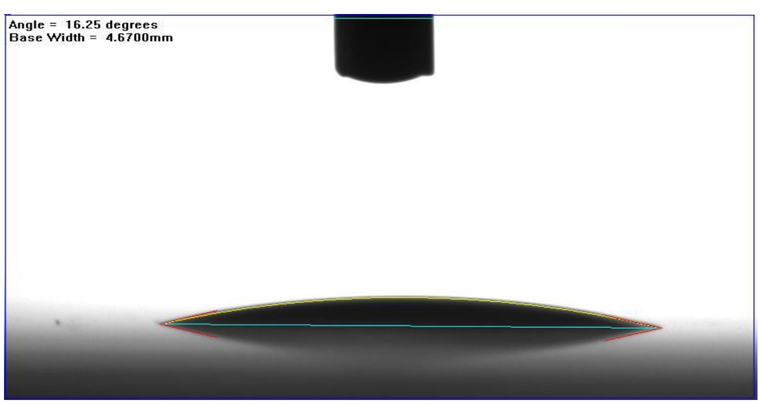

Figure 5 Water contact angle of the specimen

(e) Scanning Electron microscopy (SEM)

Figure 6 illustrated the fracture surfaces for specimens that fractured under tensile stress. The relatively smooth surface was observed as comparing with nano-reinforced composites. In a such way, we could observe varyign failure modes associated with the incorporation of nanoparticles.

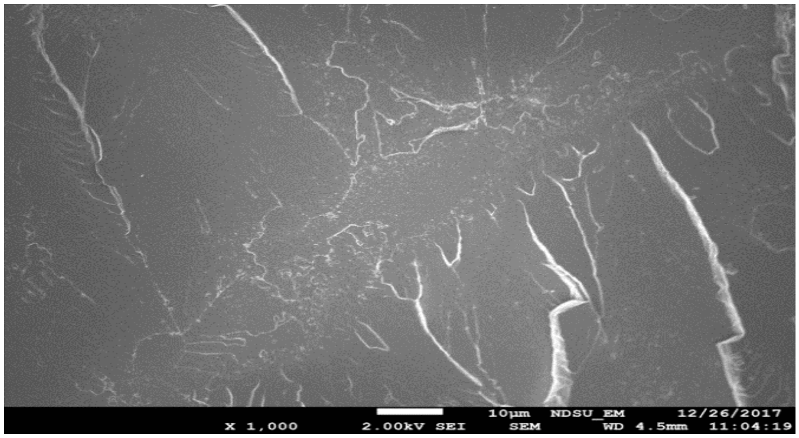

Figure 6 SEM image of fracture surface for the sample

6.3.2 Salt fog test: effects of time variant on the coating performance

Like discussed in the previous section, Potentiostatic EIS test was planned to be performed on each sample before the salt fog test, 24 hrs., 200 hrs. and 500 hrs. after the test. The impedance modulus Zmod is used to characterize the corrosion protection of the coated sample. Improving performance was observed in those nano-modified composite coatings.

6.4.1 National Conference Presentation and Poster in ND EPSCoR 2018 State Conference

The PI Dr. Lin attended the national conference: **SPIE-Smart Structures + Nondestructive Evaluation**, at Denver, Colorado, March 4-8, 2018, where he presented the group study related to this project (in his presentation slides with acknowledgment to USDOT CAAP support). The presentation topic was entitled "*Data-Driven Structural Diagnosis and Conditional Assessment: From Shallow to Deep Learning*". This work of data-enabled conditional assessment is currently funded by ND DOC, and potentially leverage our current USDOT CAAP project by providing deep understanding on performance assessment.

Two graduate students, Matthew Pearson and Xingyu Wang (see *Figure 7*), participated in the poster session in the ***ND EPSCoR 2018 State Conference*** in Grand Forks, ND, at April 17, 2018 (the poster with acknowledgment to USDOT CAAP support). Since North Dakota has become the second-leading oil-producing state in the nation and pipeline is used as one major liquid transportation, the study of this project associated with effective corrosion control of pipeline raised much attention from audience in a broader field of public, government and industry pipeline stakeholders.

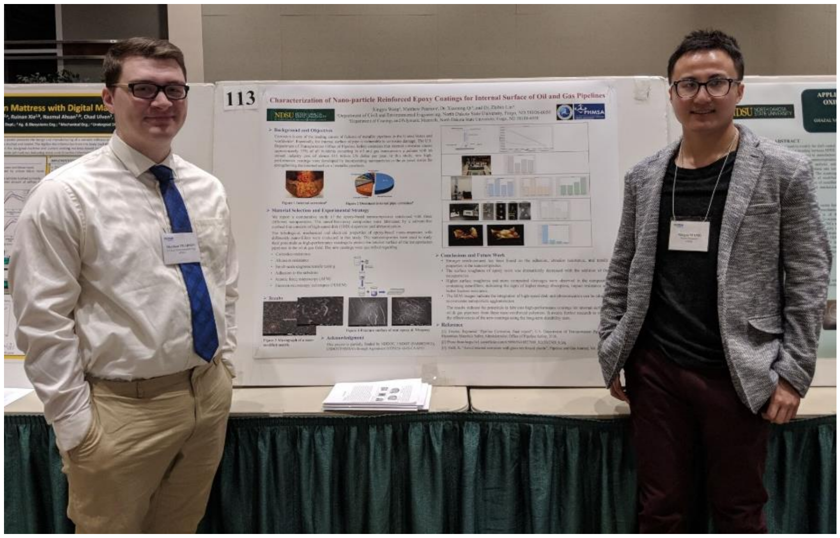

Figure 7 MS student Matthew Pearson (left) and PhD student Xingyu Wang (right) attended and presented their US DOT CAAP project in poster sesion in ND EPSCoR 2018 State Conference in Grand Forks, April 17th, 2018

6.4.2 2018 Pipeline Research & Development Forum hosted by US DOT PHMSA

The PI Dr. Lin with his two PhD students, Mingli Li and Xingyu Wang, were invited to attend and present their work in the poster session (see *Figure 8*) in the ***2018 Pipeline Research & Development Forum*** in Baltimore, MD, on Sept. 11th-12th, 2018. Travel was a great experience and a great opportunity for Dr. Lin and his PhD students to make great knowledge exchange with academic, government and industry pipeline stakeholders. Communication helped to build up a potential collaboration with other peers, and also motivated the research group to identify more real-world challenges that could further promote the corrosion control design for pipeline safety associated with this project.

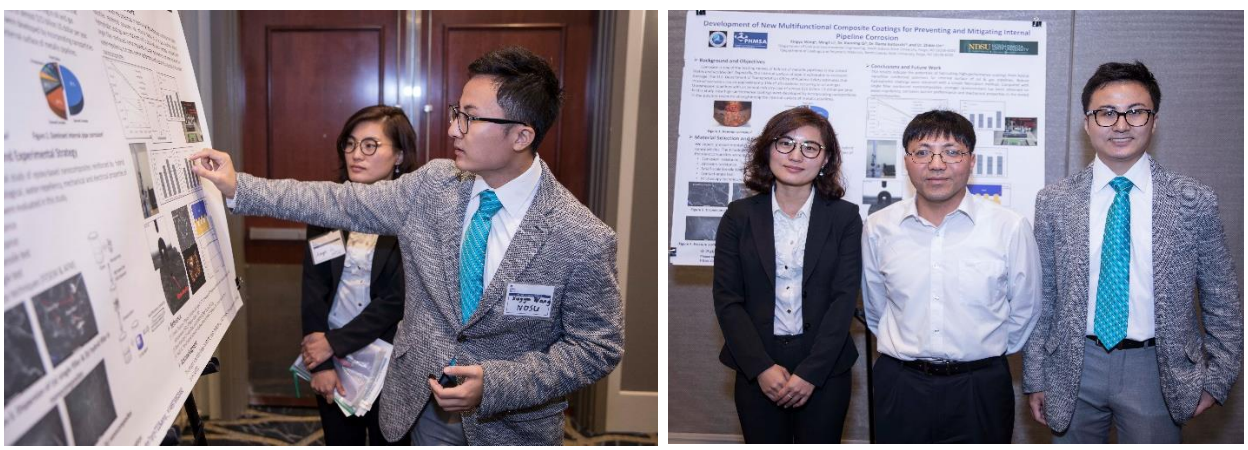

Figure 8 Two Ph.D. students Mingli Li and Xingyu Wang with their advisor Dr. Zhibin Lin attended and presented their US DOT CAAP project by posters in 2018 Pipeline Research & Development Forum hosted by US DOT PHMSA, Sept. 11th-12th, 2018

6.4.3 High school student outreach program

In this summer, as illustrated in Figs. 9-10, four high school students from North Dakota Governor's Schools program were recruited in a six-week research in Dr. Lin’s group. North Dakota Governor’s Schools is a residential program for scholastically motivated North Dakota high school sophomores and juniors. Both lecture and experiment work were conducted for the student to learn the nanoparticle modified coating synthesis, and the corrosion behaviors of metallic materials.

This outreach is be unique for Dr. Lin’s research to disseminate the current research efforts and foster the next-generation engineers to gain better understanding of the science and material, and could motivate them to pursue this area in their future career.

Figure 9 Four high school students with the graduate student in Dr. Lin’s research group for preparing coating samples and performing tests.

Figure 10 High school students presented their work when in Dr. Lin’s research group.

The following findings and discussion were revealed from the results of our experimental program:

- Significant variation between true density and bulk density can be observed for nanofillers as the value of the inter-particle void volume will be included in the measurement of bulk density. Bulk density will be used to determine the volume concentration for the nanocomposites.

- The results that obtained from Fourier Transform Infrared Spectrometer (FTIR) analysis can be summarized: the nanofillers were simply dispersed into the polymer matrix, there was no chemical reaction observed between polymer and nanofillers in the tested samples.

- Salt fog test:
  The result from this long-term test indicates that the corrosion resistance of the epoxy can be significantly increased by incorporating designed nano-modified composites.

- The air sprayed sample has stronger adhesion between coating and substrates as compared to the samples that prepared by drawdown method. However, a slight reduction of corrosion protection property was observed.

The proposed new multifunctional composite coatings are focusing on the enhancement of the three most relevant properties which are anti-corrosion, anti-fouling, and abrasion resistance. The following targets will be focused on the next step in the field performance as planned in Task 7